the hydrogenolysis of unsaturated cyclopropanes.[20] Of further interest, acid inhibits while alkali accelerates hydrogen uptake of the substrates under study. Thus hydrogenolysis at 50 p.s.i. of *trans*-epoxysuccinic acid in 0.5 *N* hydrochloric acid results in negligible hydrogen uptake. The usual effect of acid is to catalyze epoxide hydrogenolysis[3] and this effect plus other results has led to the view[3] that hydrogenolysis takes place *via* acid catalyzed ring opening to give a carbonium ion which then accepts hydrogen. It is clear that this mechanism cannot be operative in the formation of malic acid from the epoxysuccinic acids. Of further interest, the product ratio is changed on going from an aqueous solution of *trans*-epoxysuccinic acid to neutral, pH 7.0, solution.[21] At pH 7.0, malic acid is the main product, while in aqueous solution, pH 2, diglycolic acid and succinic acid are found in quantity. It would seem that with these substrates product composition is affected by acidity,[22] hydrogenolysis of both carbon–oxygen bonds, and of the carbon–carbon bond being increased in the acid solution.

From Fig. 2 it is to be seen that *threo*-2,3-dideuteriosuccinic acid[23] (IV) results from the hydrogenolysis of *trans*-epoxysuccinic acid (V), the deuterium atoms having added in a *cis* fashion and, presumably, displacing by backside attack the oxygen atom of the epoxide. This latter point, of course, cannot be established conclusively from the present data. *cis*-Epoxysuccinic acid (I), on the other hand, yielded a 1:1 mixture of *erythro*-2,3-dideuteriosuccinic acid (III) and *threo*-2,3-dideuterioscuccinic acid (IV). The mixture of stereoisomers of dideuteriosuccinic acid obtained from epoxysuccinic acid cannot be attributed to racemization of the product, *erythro*-2,3-dideuteriosuccinic acid, expected on the basis of *cis*-hydrogen addition, since the same mixture was found on incomplete hydrogenolysis[24] and also racemization of *erythro*-2,3-dideuteriosuccinic acid did not occur in a control experiment. Another possible explanation for the mixture of stereoisomers, the racemization of *cis*-epoxysuccinic acid to *trans*-epoxysuccinic acid prior to hydrogenolysis is ruled out by the steric purity of the *threo*-3-deuterio-DL-malic acid obtained from the *cis*-epoxysuccinic acid. It would thus seem that with *cis*-epoxysuccinic acid hydrogenolysis occurs by both *cis* and *trans* addition of deuterium or, more likely, that some half-hydrogenated state[25] may exist in two configurations which yield, on completion of hydrogenation by *cis* addition, both isomers of 2,3-dideuteriosuccinic acid.

**Acknowledgment.**—This research was supported, in part, by research grant GM 06245 from the Division of General Medical Sciences, Public Health Service.

(20) E. F. Ullman, *J. Am. Chem. Soc.*, **81**, 5389 (1959).

(21) The approximate $pK_1$ and $pK_2$ values of *cis*-epoxysuccinic acid and *trans*-epoxysuccinic acid are 2.2, 3.7, and 2.2, 3.2, respectively (unpublished work of O. Gawron and T. P. Fondy).

(22) In a preliminary experiment, hydrogenolysis at 50 p.s.i. of *trans*-epoxysuccinic acid in glacial acetic acid resulted in 40% hydrogen uptake after 48 hr. Analytical chromatography did not demonstrate any malic or diglycolic acids and presumably, succinic acid was formed. Tartaric acid was not apparent.

(23) However, the possibility that several percent of the *erythro* isomer is present can not be excluded by the spectrophotometric technique.

(24) Two grams of *cis*-epoxysuccinic acid in 30 ml. of deuterium oxide was hydrogenolyzed for one hour with 0.26 g. of catalyst at an initial deuterium pressure of 40 p.s.i. to yield 83 mg. (4.5%) of succinic acid.

(25) I. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

# Stepwise Reduction of *gem*-Dihalocyclopropanes with Tri-*n*-butyltin Hydride[1]

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*Received November 7, 1962*

The reduction of substituted *gem*-dibromocyclopropanes to monobromocyclopropanes can be effected in good yield with tri-*n*-butyltin hydride at temperatures below 40°. This radical reaction gives a mixture of isomers in most of the cases where one has the possibility of forming *cis* and *trans* isomers. A tentative assignment of structure of some of the isomer pairs (*e.g.*, *cis*- and *trans*-7-bromobicyclo[4.1.0]heptane) is made on the basis of n.m.r. data. Preferential reduction of 7-bromo-7-chlorobicyclo[4.1.0]heptane to the chlorocyclopropane is easily accomplished under these conditions. Reduction of 7,7-dichlorobicyclo[4.1.0]heptane with tri-*n*-butyltin hydride requires temperatures of *ca.* 140°. The partial reduction of bromoform, tribromofluoromethane, carbon tetrachloride, and chloroform by tri-*n*-butyltin hydride is reported.

Our recent work[3] on the preparation of cyclopropyltin compounds *via* cyclopropylmagnesium bromide made a study of substituted cyclopropyltin compounds of interest to us. Such a study required the corresponding cyclopropyl bromides, and this paper reports the preparation of such bromides by the reduction of the readily accessible *gem*-dibromocyclopropanes[4,5] with tri-*n*-butyltin hydride.

The reduction of organic halides to the corresponding hydrocarbons by organotin hydrides,

$$R_3SnH + R'X \longrightarrow R_3SnX + R'H$$

was discovered by van der Kerk, *et al.*[6] Several examples of this reaction have been described since then.[7-9] Kuivila[9] has reported the stepwise reduction

(1) Presented at the Symposium on Organometallic Compounds sponsored by the Inorganic Chemistry Div., Chemical Institute of Canada, and the University of British Columbia, Vancouver, B. C., September 4–6, 1962.

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(3) D. Seyferth and H. M. Cohen, *Inorg. Chem.*, **1**, 913 (1962).

(4) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956).

(5) D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962).

(6) G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.* (London), **7**, 356 (1957).

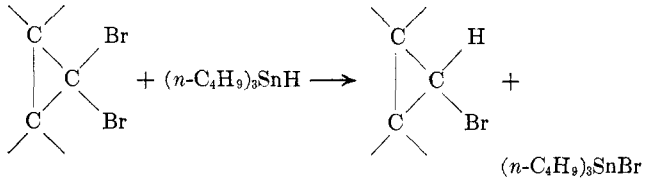
(7) L. A. Rothman and E. I. Becker, *J. Org. Chem.*, **25**, 2203 (1960).

(8) (a) E. J. Kupchik and R. E. Connolly, *ibid.*, **26**, 4747 (1961); (b) E. J. Kupchik and R. J. Kiesel, *Chem. Ind.* (London), 1654 (1962).

(9) H. G. Kuivila, Organic Chemistry Colloquium, Harvard University, February 28, 1961; H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Am. Chem. Soc.*, **84**, 3584 (1962).

of benzotrichloride to toluene ($C_6H_5CCl_3 \rightarrow C_6H_5CHCl_2 \rightarrow C_6H_5CH_2Cl \rightarrow C_6H_5CH_3$) in good yield using tri-*n*-butyltin hydride, and has presented convincing evidence that such reductions are radical reactions.

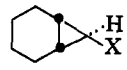
We have found that tri-*n*-butyltin hydride undergoes an exothermic reaction with *gem*-dibromocyclopropanes, and that good (70–85%) yields of substituted cyclopropyl bromides are produced when the reaction is moderated so as to keep the temperature below 40°.



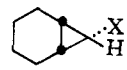

The chemical shift of the protons introduced in these reactions in all cases is at high field, 2.58–3.23 p.p.m. downfield from tetramethylsilane, and this is in agreement with a retention of the cyclopropane structure in this reaction.[10]

The reduction of 7,7-dibromobicyclo[4.1.0]heptane resulted in a mixture of both possible isomers in a ratio of 2.5:1, which is in accord with the finding[9] that tin hydride–organic halide reactions are radical processes.

An unambiguous assignment of structure to the two 7-bromobicyclo[4.1.0]heptane isomers formed in this reaction (and to other isomer pairs formed in the reduction of other *gem*-dihalocyclopropanes during the course of this study) is not possible at this time. In both isomers, which could be separated by gas chromatography, the cyclopropane hydrogens gave an $A_2X$ system in the n.m.r. spectrum with differing values of $J_{AX}$: 3.7 c.p.s. for the isomer obtained in smaller yield and 8.0 c.p.s. for the other isomer. In most known cases the *cis* coupling constants in cyclopropane systems are larger than the *trans* coupling constants.[10,11] However, in substituted 1-chlorocyclopropanes, obtained by the organolithium–methylene chloride–olefin reaction, Closs and Closs[12] have claimed that the *trans* coupling constants are larger than the corresponding *cis* coupling constants. Schöllkopf and Lehmann[10] have reported the preparation of a 2:1 mixture of the isomers of 7-phenylmercaptobicyclo[4.1.0]heptane in the reaction of chloromethyl phenyl sulfide, *n*-butyllithium and cyclohexene. Considerations based on the assumption of a carbene mechanism led them to assign the *trans* configuration to the isomer formed in higher yield, which had the larger coupling constant, $J_{AX}$. The structural assignments of Closs and Closs also were based on the assumption that their reaction proceeded *via* a carbene intermediate. It must be mentioned that these assignments are contrary to the theoretical treatment by Karplus[13], which has been confirmed experimentally by Hutton and Schaefer.[11a] Furthermore, it is not completely certain that in the above cases a carbene mechanism is operative,[14] and for these reasons we prefer to follow the rule rather than its two exceptions. This would lead to an assignment of the *trans* structure Ia to the 7-bromobicyclo[4.1.0]heptane isomer formed in lesser yield ($J_{AX}$ = 3.7 c.p.s.) and of the *cis* structure IIa to the other isomer with $J_{AX}$ = 8.0 c.p.s.[12b]

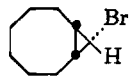



Ia. X = Br
b X = Cl



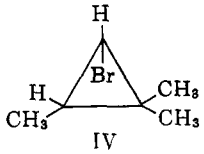

IIa. X = Br
b. X = Cl

In terms of the evidence presented[16] that the 2-methylcyclopropyl free radical is either planar about the 1-position or inverts its configuration rapidly, we may picture our reaction in the following manner on the basis of our structural assignments. Attack by the bulky tri-*n*-butyltin radical would be expected to occur at the less hindered C-Br bond, which is *cis* with respect to the two cyclopropane hydrogens of 7,7-dibromobicyclo[4.1.0]heptane. Attack by tri-*n*-butyltin hydride on the resulting radical (leading to product and a new tri-*n*-butyltin radical) then would occur, with the hydride having the possibility of attacking on either side of the cyclopropyl ring. In terms of either a planar or a rapidly inverting radical center, steric factors hindering approach of the bulky tri-*n*-butyltin hydride seem to outweigh all other considerations in view of the observed *cis–trans* ratio in the product. However, in view of the fact that the *cis–trans* ratio is only 2.5, steric factors do not result in a stereospecific reaction. It is interesting to note that an increase in size of the ring fused to the cyclopropane system does seem to lead to a stereospecific reaction. The n.m.r. spectrum of the monobromo compound derived from 9,9-dibromobicyclo[6.1.0]nonane in 84% yield showed the presence of only one isomer, which according to the discussion above, would be III, since $J_{AX}$ was 7.5 c.p.s. Steric factors may be sufficient to explain this observation, but a transannular, stereospecific hydrogen abstraction by the cyclopropyl radical, followed by introduction of the tin hydride derived hydrogen into the $C_6$ bridge, may also be considered as a possibility.

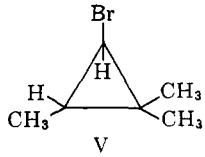



III

An isomer mixture of IV ($J_{AX}$ = 7.2 c.p.s.) and V ($J_{AX}$ = 3.8 c.p.s.) was obtained from 1,1-dibromo-2,2,3-




IV




V

trimethylcyclopropane, with the ratio of IV to V being 4:1 as determined from the n.m.r. spectrum. Two isomers were obtained when 1,1-dibromo-2-vinylcyclopropane was treated with tri-*n*-butyltin hydride, but no

(10) U. Schöllkopf and G. J. Lehmann, *Tetrahedron Letters*, 165 (1962), and references cited therein.

(11) (a) H. M. Hutton and T. Schaefer, *Can. J. Chem.*, **40**, 875 (1962); (b) J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962).

(12) (a) G. L. Closs and L. E. Closs, *ibid.*, **82**, 5723 (1960). (b) NOTE ADDED IN PROOF. Since the submission of this manuscript the structural assignment of Closs and Closs[12] have been corrected; G. L. Closs, R. A. Moss, and J. J. Coyle, *J. Am. Chem. Soc.*, **84**, 4985 (1962).

(13) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); H. S. Gutowsky, M. Karplus, and D. M. Grant, *ibid.*, **31**, 1278 (1959); M. Karplus, *J. Phys. Chem.*, **64**, 1793 (1960).

(14) Recent work of Franzen[15a] and Hoberg[15b] suggests that such reactions could involve addition of an organolithium intermediate to the olefin, followed by γ-elimination to form the cyclopropane isolated.

(15) (a) V. Franzen, *Chem. Ber.*, **95**, 1964 (1962); (b) H. Hoberg, *Ann.*, **656**, 1 (1962).

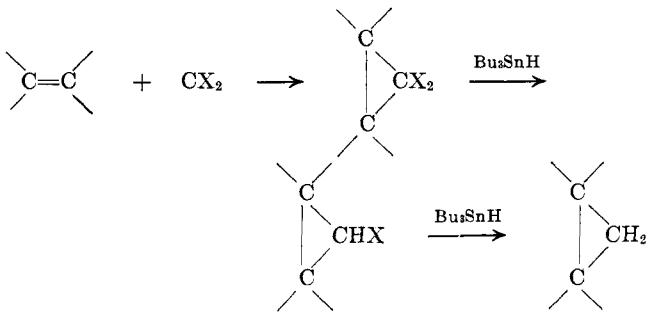
(16) D. E. Applequist and A. H. Peterson, *J. Am. Chem. Soc.*, **82**, 2372 (1960).

assignments could be made on the basis of their n.m.r. spectra.

The replacement of one of the chlorine atoms of 7,7-dichlorobicyclo[4.1.0]heptane by hydrogen required heating this halide with one molar equivalent of tri-*n*-butyltin hydride at 140°. As in the case of the dibromo-analog, a mixture of isomers (83% yield), IIb and Ib in 1.8:1 molar ratio, resulted. Again, assignment of these structures is based on the correlation of the larger coupling constant in the cyclopropane system with the *cis* structure. Preferential reduction of the C-Br bond in 7-bromo-7-chlorobicyclo[4.1.0]heptane could be effected with ease, giving a mixture of IIb and Ib (2.5:1 molar ratio) in 97% yield. Kuivila[9] has reported that organic bromides are much more reactive toward organotin hydrides than are the corresponding chlorides, an observation readily understandable in terms of the radical mechanism of these reactions.

Complete reduction to the cyclopropane also was easily accomplished. Thus, in one example examined, 1,1-dibromo-2,2,3,3-tetramethylcyclopropane was converted by two molar equivalents of tri-*n*-butyltin hydride to 1,1,2,2-tetramethylcyclopropane in 69% yield.

The reaction sequence




thus represents a convenient, high-yield route to many substituted cyclopropyl bromides and chlorides and to substituted cyclopropanes. It must be borne in mind, however, that organotin hydrides can react with other organic functions, such as the carbonyl group in aldehydes and ketones[17] and olefinic and acetylenic unsaturation,[6,18] and that for this reason the reduction reaction reported by us may not be of completely general applicability. The reduction of 1,1-dibromo-2-vinylcyclopropane shows that tri-*n*-butyltin hydride will react preferentially with the C-Br bond in the presence of an unactivated olefinic linkage.

Alternate routes, based on reduction of *gem*-dihalocyclopropanes, to halocyclopropanes and to cyclopropanes are available. Thus it has been reported[19] that reduction of 3,3-dibromocyclopropane-*cis*-1,2-diacetic acid by zinc dust in glacial acetic acid or by hydrogenation over platinum in methanolic potassium hydroxide gave the monobromo compound in 50% yield. Complete substitution of halogen by hydrogen in *gem*-dihalocyclopropanes can be effected by sodium in ethanol,[20] by lithium/*tert*-butyl alcohol in ethylene glycol dimethyl ether,[21] or by catalytic hydrogenation over Raney nickel in methanolic potassium hydroxide.[19]

(17) H. G. Kuivila and O. F. Beumel, Jr., *J. Am. Chem. Soc.*, **80**, 3798 (1958); **83**, 1246 (1961).

(18) G. J. M. van der Kerk and J. G. Noltes, *J. Appl. Chem.* (London), **9**, 106 (1959).

(19) K. Hofmann, S. F. Orochena, S. M. Sax, and G. A. Jeffrey, *J. Am. Chem. Soc.*, **81**, 992 (1959).

(20) W. von E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6164 (1954).

(21) I. M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 1689 (1962).

We also have examined the reduction of some polyhalomethanes with tri-*n*-butyltin hydride. Carbon tetrachloride was converted to chloroform (85% yield) and chloroform to methylene chloride (94% yield) by this procedure. Bromoform was reduced to methylene bromide (62%) and tribromofluoromethane to dibromofluoromethane (69%) by the tin hydride. In the latter two reactions the yield of tri-*n*-butyltin bromide was around 95%, and the difference in the yield between the reduced polyhalomethane products and the tri-*n*-butyltin bromide is due to some further reduction of the products to methyl bromide and bromofluoromethane, respectively. Since this work was completed, a similar stepwise reduction of carbon tetrachloride with triphenyltin hydride has been reported.[22]

## Experimental[23]

**Preparation of Starting Materials.**—Tri-*n*-butyltin hydride[24] and *gem*-dibromocyclopropanes[4,5] were prepared by methods described in the literature. 7,7-Dichlorobicyclo[4.1.0]heptane was obtained by the procedure of Doering and Hoffmann[20] and 7-bromo-7-chlorobicyclo[4.1.0]heptane by our recently reported[25] method.

**Preparation of Substituted Bromocyclopropanes from *gem*-Dibromocyclopropanes.**—The reaction of 7,7-dibromobicyclo[4.1.0]heptane with tri-*n*-butyltin hydride is described as an example of the procedure used.

In a 100-ml., three-necked flask equipped with a thermometer, a magnetic stirrer and a pressure-equalizing dropping funnel topped with a nitrogen inlet tube was placed 20.3 g. (0.08 mole) of 7,7-dibromobicyclo[4.1.0]heptane. To this was added dropwise 23.2 g. (0.08 mole) of tri-*n*-butyltin hydride with stirring under nitrogen during 1 hr. The temperature was maintained below 40° by external cooling. After the addition had been completed, the mixture was stirred at *ca.* 30° for another hour. Distillation at reduced pressure gave two fractions: (1) 13.24 g., boiling range 94–109° at 25–27 mm.; (2) 29.2 g., b.p. 98–100° at 0.3 mm., $n^{25}D$ 1.5029. Fraction 2 was essentially pure tri-*n*-butyltin bromide (99% yield) (lit.,[26] b.p. 120° at 1.8 mm., $n^{25}D$ 1.5022). Fraction 1 was fractionally distilled to give 11.4 g. (82%) of 7-bromobicyclo[4.1.0]heptane, b.p. 96–99° at 36 mm., 78° at 16 mm., $n^{25}D$ 1.5137.

*Anal.* Calcd. for $C_7H_{11}Br$: C, 48.02; H, 6.33; Br, 45.65. Found: C, 48.15; H, 6.49; Br, 45.78.

Gas chromatographic analysis showed the presence of two components in the redistilled fraction, in 1:2.5 molar ratio in order of increasing retention time: (a) $n^{25}D$ 1.5099; % Br, 45.58; n.m.r.,[27] complex multiplets from 0.9–1.4 and 1.4–2.2 p.p.m., triplet at 2.58 p.p.m. ($J$ = 3.7 c.p.s.); (b) $n^{25}D$ 1.5182; % Br, 45.96; n.m.r.: complex multiplet from 0.9–2.4 p.p.m., triplet at 3.19 p.p.m. ($J$ = 8.0 c.p.s.).

In a similar manner the following compounds were prepared.

**1-Bromo-2,2-dimethylcyclopropane**, 82% yield; b.p. 107–108°; $n^{25}D$ 1.4516; n.m.r.: quartets at 0.6 and 0.93 p.p.m., two singlets at 1.12 and 1.24 p.p.m., quartet at 2.64 p.p.m.

*Anal.* Calcd. for $C_5H_9Br$: C, 40.30; H, 6.09; Br, 53.61. Found: C, 40.30; H, 6.11; Br, 53.34.

**1-Bromo-2,2,3-trimethylcyclopropane**, 79% yield; b.p. 61–62° at 70 mm., $n^{25}D$ 1.4593; n.m.r.: complex multiplet from 0.82–1.8 p.p.m., doublet at 2.77 p.p.m. ($J$ = 3.8 c.p.s., assumed to be due to the *trans* isomer V), doublet at 3.23 p.p.m. ($J$ = 7.2 c.p.s., assumed to be due to the *cis* isomer IV). The area ratio of these doublets gave a *cis:trans* ratio of 4:1.

*Anal.* Calcd. for $C_6H_{11}Br$: C, 44.19; H, 6.80; Br, 49.01. Found: C, 44.55; H, 6.98; Br, 48.98.

(22) D. H. Lorenz and E. I. Becker, *J. Org. Chem.*, **27**, 3370 (1962).

(23) All reactions were carried out under an atmosphere of prepurified nitrogen. Analyses by Dr. S. M. Nagy (M.I.T.), the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and A. Schoeller, Kronach, Ofr.

(24) G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.* (London), **7**, 366 (1957).

(25) D. Seyferth and J. M. Burlitch, *J. Am. Chem. Soc.*, **84**, 1757 (1962).

(26) D. Seyferth, *ibid.*, **79**, 2133 (1957).

(27) N.m.r. spectra were recorded in carbon tetrachloride solution using a Varian Associates A60 n.m.r. spectrometer. Chemical shifts are given in parts per million downfield from tetramethylsilane.

Attempted separation of the isomers by gas chromatography (Dow Corning 710 silicone fluid on Chromosorb P, 70° jacket temp., 15 p.s.i. He) was not successful, only partial resolution being obtained.

**1-Bromo-2,2,3,3-tetramethylcyclopropane**,[28] 78% yield; b.p. 51° at 22 mm.; $n^{25}D$ 1.4652; n.m.r.: doublet at 1.08 p.p.m., singlet at 2.63 p.p.m.

*Anal.* Calcd. for $C_7H_{13}Br$: C, 47.47; H. 7.40; Br, 45.13. Found: C, 47.80; H, 7.30; Br, 45.47.

**9-Bromobicyclo[6.1.0]nonane**, 84% yield, b.p. 40–42° at 0.13 mm., $n^{25}D$ 1.5142; n.m.r.: complex multiplet from 0.5–2.35 p.p.m., triplet at 3.14 p.p.m. ($J$ = 7.5 c.p.s.).

*Anal.* Calcd. for $C_9H_{15}Br$: C, 53.22; H, 7.44; Br, 39.34. Found: C, 53.35; H, 7.52; Br, 39.45.

**1-Bromo-2-phenylcyclopropane**, 71% yield; b.p. 48–50° at 0.15 mm.; $n^{25}D$ 1.5696. A mixture of isomers is to be expected in this case, but the n.m.r. spectrum did not provide any information on this question, since the absorption from 2.7–3.4 p.p.m. was a 13 peak multiplet.

*Anal.* Calcd. for $C_9H_9Br$: C, 54.85; H, 4.60; Br, 40.55. Found: C, 55.05; H, 4.79; Br, 40.86.

**1-Bromo-2-vinylcyclopropane**, 62% yield; boiling range 62–74° at 90 mm., collected in two fractions: (1) 8.0 g., b.p. 62–69° at 95–90 mm., $n^{25}D$ 1.4887, and (2) 1.9 g., b.p. 69–74° at 90 mm., $n^{25}D$ 1.4956. Gas chromatographic analysis showed three components in fraction 1: in order of increasing retention time, A, B, and C in a ratio of 1:3.1:6.3. Fraction 2 contained B and C in *ca.* 1:12 molar ratio. All three compounds were collected by gas chromatography. Compound A, $n^{25}D$ 1.4596, (C, 35.04; H, 5.26) remained unidentified and may have been due to impurities in the butadiene used to prepare 1,1-dibromo-2-vinylcyclopropane. Compounds B and C are the expected isomers of 1-bromo-2-vinylcyclopropane. Compound B, $n^{25}D$ 1.4885; n.m.r.: complex multiplets at 0.8–1.45 and 1.45–2.25 p.p.m., octet at 2.7 p.p.m., complex vinyl absorption at 4.8–5.8 p.p.m.

*Anal.* Calcd. for $C_5H_7Br$: C, 40.84; H, 4.80; Br, 54.36. Found: C, 40.55; H, 4.93; Br, 54.86.

Compound C, $n^{25}D$ 1.4953, n.m.r.: complex multiplet from 0.5–1.9 p.p.m., sextet at 3.03 p.p.m., complex vinyl absorption from 4.9–5.9 p.p.m.

*Anal.* Found: C, 41.00; H, 4.86; Br, 54.75.

No assignment of structure could be made on the basis of the n.m.r. data. Isomers B and C were formed in 17 and 45% yield, respectively (ratio 1:2.6), on the basis of gas chromatographic analysis of fractions 1 and 2. The preponderance of the isomers in which the cyclopropane hydrogens are *cis* to one another in the other cases leads to the suggestion that B is the *trans* isomer and C is the *cis* isomer. The infrared spectra of both isomers showed a strong band due to the C=C linkage at 1637 cm.$^{-1}$.

**Reduction of 7-Bromo-7-chlorobicyclo[4.1.0]heptane.**—The procedure described above was used in the reaction of 0.05 mole each of 7-bromo-7-chlorobicyclo[4.1.0]heptane and tri-*n*-butyltin hydride at *ca.* 0°. 7-Chlorobicyclo[4.1.0]heptane, b.p. 56–58° at 11 mm., $n^{25}D$ 1.4861, was obtained in 97% yield, and tri-*n*-butyltin bromide in 96% yield.

*Anal.* Calcd. for $C_7H_{11}Cl$: C, 64.36; H, 8.49; Cl, 27.15. Found: C, 64.30; H, 8.08; Cl, 27.46.

Gas chromatographic analysis showed the presence of IIb and Ib in 2.5:1 ratio. Both were isolated by gas chromatography; IIb: $n^{25}D$ 1.4890; n.m.r., complex multiplet from 0.9–2.4 p.p.m., triplet at 3.14 p.p.m. ($J$ = 7.5 c.p.s.). Ib: $n^{25}D$ 1.4807; n.m.r., complex multiplets from 1.0–1.5 p.p.m. and 1.5–2.2 p.p.m., triplet at 2.56 p.p.m. ($J$ = 3.7 c.p.s.).

**Reduction of 7,7-Dichlorobicyclo[4.1.0]heptane.**—Since a mixture of 0.08 mole of 7,7-dichlorobicyclo[4.1.0]heptane and 0.08 mole of tri-*n*-butyltin hydride did not react under the conditions described above, it was heated at 140° for 3 hr. Distillation gave 8.65 g. (83%) of a 1.8:1 mixture of IIb and Ib, b.p. 56–58° at 11 mm., $n^{25}D$ 1.4860, and 23.6 g. (91%) of tri-*n*-butyltin chloride, b.p. 80–83° at 0.07 mm., $n^{25}D$ 1.4894 (lit.,[29] $n^{22}D$ 1.4908).

**Complete Reduction of 1,1-Dibromo-2,2,3,3-tetramethylcyclopropane.**—Tri-*n*-butyltin hydride (0.1 mole) was added dropwise to 0.05 mole of 1,1-dibromo-2,2,3,3-tetramethylcyclopropane in 10 ml. of pentane at 0°. The reaction mixture was kept at room temperature for 3 days. Distillation gave 3.4 g. (69%) of 1,1,2,2-tetramethylcyclopropane, b.p. 75.5–76°, $n^{25}D$ 1.3982 (lit.,[30] b.p. 73–74°, $n^{25}D$ 1.3955).

**Reduction of Polyhalomethanes.**—These reactions were carried out in a similar manner to those described for the *gem*-dibromocyclopropanes. The reaction temperature was maintained at 0° during and for 10 min. after the addition of the hydride (0.02 mole) to the polyhalomethane (0.04 mole), then was allowed to stay at room temperature for 10 min. before distillation of the reaction mixture. The halomethane fraction was analyzed by gas chromatography, and the yields reported in the discussion were obtained. In each case minor amounts of more volatile by-products were present, presumably due to further reduction of the expected product by tri-*n*-butyltin hydride. Products were identified by retention times, infrared spectra, and/or refractive indices. The isolated yield of tri-*n*-butyltin bromide or chloride was *ca.* 95% in each case.

**Acknowledgment.**—This work was supported in part by the United States Air Force under contract no. AF 33(657)-8532, monitored by the Materials Central, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. The authors are indebted to Mr. R. J. Minasz for samples of 7-bromo-7-chloro- and 7,7-dichlorobicyclo[4.1.0]heptane, to the Metal & Thermit Corp. for a gift of tri-*n*-butyltin chloride, to the Houdry Process and Chemical Co. for a sample of tetramethylethylene, and to Cities Service Research and Development Co. for a sample of cycloöctene.

(28) Since 1,1-dibromo-2,2,3,3-tetramethylcyclopropane is a solid, this reaction was carried out (0.07-mole scale) in 25 ml. of pentane.

(29) Z. M. Manulkin, *Zh. Obshch. Khim.*, **18**, 299 (1948).

(30) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).